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EXPLORATORY STUDY OF FACTORS AFFECTING AEROSOL FORMATION

David F. Miller

Battelle Columbus Laboratories

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November 1974

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16. ABSTRACT

A smog chamber study was completed to provide methodology and preliminary data on the rate of photooxidation of SO_2 in environments simulating urban atmospheres. The experimental program included irradiation testing of clean air as well as air containing pollutants at concentration levels typical of those found in urban atmospheres. Results showed the rate of SO_2 photooxidation to be unexpectedly as high as 5% per hour. Furthermore, the presence of deliberately injected pollutants did not seem to have a decisive effect on the SO_2 photooxidation.

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FOREWORD

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INTRODUCTION

Numerous aerometric studies have shown that sulfuric acid and sulfate aerosols constitute a substantial fraction of the aerosol matter existing in both urban and rural areas throughout the United States. Compositional analyses of size-fractionated aerosols reveal that most of the sulfate-type aerosol is in the particle-size range below 2 μm in diameter.[1]* A more recent study in New York by our group showed that 90 percent of the sulfate is in this size range and that sulfate alone comprises 15-25 percent of the total mass of aerosol < 2 μm in diameter.[2] In addition to adverse visibility conditions associated with aerosols of this size range, it is well established that such aerosols are highly respirable, and the results of an extensive community health (CHESS) program indicate that a substantial relationship exists between sulfate levels and some types of morbidity, even at sulfate levels of 8-12 $\mu g/m^3$ (corresponding to conversion of only 2-3 ppb SO_2).

Interpreting data from the U. S. National Air Surveillance Networks, Altshuller concludes that sulfate-bearing aerosols are widely distributed throughout the U.S.[3] Furthermore, the occurrence of sulfate appears to be largely due to chemical reactions in the atmosphere (as opposed to emitted sulfate), and there is considerable evidence that long-distance transport of SO_2 from urban areas concomitant with SO_2 oxidation is responsible for a "residual" sulfate level of nearly 5 $\mu g/m^3$ throughout many of the eastern states. Altshuller's analyses of atmospheric data also indicated that the relationship between SO_2 and sulfate concentrations is non-linear and, presumably, complex.

To help EPA develop effective control strategies for limiting the sulfate aerosol concentrations, the predominant and hopefully controllable factors affecting the rate of SO_2-to-sulfate conversion must be known. This report presents pertinent details and results of an investigation in which a smog-chamber approach is being taken to study SO_2 oxidation in simulated atmospheres. The EPA is continuing to support research on this problem at Battelle and at other laboratories as well.

* References appear on page 21

BACKGROUND

The rate of SO_2 oxidation in the atmosphere, particularly over relatively short times, is difficult to measure due to variety and variability of SO_2 emissions and inadequate tracers thereof. On a more simplified yearly basis, Junge[4] estimates a mean lifetime for industrially emitted SO_2 of 4-7 days, corresponding to a first-order-removal rate of about 0.6-1 percent/hr.

Using an air-trajectory technique and a diffusion model, Roberts and Friedlander[5] have made some preliminary determinations of short-term SO_2-oxidation rates in the polluted air near Los Angeles; hourly average oxidation rates during afternoon hours ranged from 2-13 percent/hr. In the study cited, there were some indications the oxidation rate was related to parameters such as O_3, free radicals, olefins, and relative humidity.

A pilot study in New York City aimed at discerning any interrelationship between SO_2 concentrations and oxidant production indicated (in a limited number of tests) that the SO_2 conversion rate was < 5 percent/hr when early morning air was irradiated naturally in Teflon (du Pont) bags throughout the day.[6] Furthermore, the SO_2 loss rate seemed unaffected by ambient particulate concentrations and was relatively constant throughout the daylight hours, with no obvious change during O_3 production.

Consistently good correlations of atmospheric sulfate concentrations with ammonium concentrations have led to the idea that NH_3 and SO_2 combine to form an addition compound in the presence of water.[4,7] Thus far, however, there is no kinetic data to support the addition-compound theory for SO_2 oxidation, and this, as well as other theories of heterogeneous SO_2 oxidation in water droplets, are questionable in that atmospheric data show an apparent dependence of the sulfate concentration on the concentration of water vapor in the air rather than on the degree of water saturation.[1] In short, although there seems to be general agreement that most of the SO_2 in the atmosphere is ultimately oxidized to sulfate-type aerosols, no consistent evidence exists from field studies to suggest explicit factors dominating the SO_2 oxidation rate.

The numerous laboratory studies likewise leave many unanswered questions regarding the detailed mechanisms and rates of sulfate formation. It is commonly held that both heterogeneous and homogeneous processes occur, and there is an abundance of data to indicate that the homogeneous rate of conversion of SO_2 to sulfate is enhanced in polluted atmospheres. A thorough review of the laboratory work on this subject through 1970 has been presented by Bufalini.[8]

Prior to 1970, many studies were conducted of SO_2 photooxidation in the first strong absorption band of SO_2. A large discrepancy existed regarding the importance of this process, as reported quantum yields for SO_2 disappearance varied from 10^{-3} to 10^{-1} molecule per quantum absorbed. Reinvestigating the reaction in 1972, Allen, et al.[9], reported an SO_2 quantum efficiency of about 6×10^{-3}. In the same year, Cox[10] reported a much lower ϕ_{SO_2} value of 3×10^{-4}. In both reports, there was some evidence of ϕ_{SO_2} dependency on SO_2 and/or O_2 concentrations, but such dependency was readily dismissed as experimental artifact. If ϕ_{SO_2} is as low as 3×10^{-4}, then, indeed, SO_2 photooxidation is an insignificant mechanism of SO_2 removal, even on a global basis. Combining $\phi_{SO_2} = 3 \times 10^{-4}$ with the specific solar ($Z = 40°$) absorption rate for SO_2 of ~0.7 hr^{-1}[11], a maximum photooxidation rate of about 0.02 percent/hr and an SO_2 mean lifetime > 200 days result.

At the time of Bufalini's review, numerous smog-chamber-type studies had demonstrated that homogeneous oxidation of SO_2 occurred at widely varying rates. In spite of all the macroscopic

evidence of enhanced oxidation, little mechanistic and kinetic information was available on intermediates specifically responsible for the conversion. In the past few years, however, quantitative rate data have been reported for HO_2[12], HO[13], and "zwitterion"[14] reactions with SO_2. Considering these as well as other pertinent reactions in computer simulations of photochemical smog, Calvert[15a,b] has estimated the homogeneous rate of SO_2 oxidation in smog to range between 1.5 and 4.7 percent/hr.* Thus, with the tools of computer simulations of reaction kinetics combined with smog-chamber data of the disappearance and formation of reactants and products, there is considerable promise that the homogeneous pathways of SO_2 oxidation in the atmosphere will soon be sufficiently understood. That is the approach and the goal of this program. With sufficient knowledge, it should then be possible to assess the significance of the homogeneous processes occurring in the atmosphere and thereby consider the value of various sulfate control strategies.

SCOPE OF PROGRAM

The ultimate objective of this program is to provide EPA with smog-chamber data useful in developing models of the conversion of SO_2 to sulfuric acid and other sulfur-bearing aerosols in polluted atmospheres. This first year of effort was devoted to defining experimental conditions and analytical techniques which would permit measuring the conversion using the smog-chamber approach. Upon establishing experimental and analytical procedures, a factorial series of experiments was conducted in which SO_2 was irradiated in air containing variable concentrations of propylene, NO_x, and H_2O vapor.

It was also observed that SO_2 oxidation was appreciable during irradiations in relatively clean air. Thus, additional experiments were conducted in small and large smog chambers and under different irradiation conditions to ascertain the conditions conducive to SO_2 oxidation in unpolluted air.

OBSERVATIONS AND TENTATIVE CONCLUSIONS

The rate of SO_2 conversion to aerosols ranged from 0.4 to 5.8 percent/hr over a wide variety of environmental conditions approaching both clean and highly polluted air. There was no evidence to suggest that the amount and/or nature of the experimental surfaces employed in the study seriously affected the observed oxidation rates; nevertheless, the existence of a surface effect was not ruled out.

In air contaminated with propylene, NO_x, and SO_2, an interaction effect on SO_2 oxidation was observed between relative humidity and the HC/NO_x ratio. At 60 percent relative humidity, high propylene/NO_x ratios resulted in higher overall (4-hr avg) SO_2 oxidation rates as well as enhanced NO oxidation. At relative humidities of 40 percent, doubling the HC/NO_x ratios resulted in little change in the overall SO_2 oxidation rates in spite of a nearly two-fold increase in the NO oxidation rate. It appears that the varying SO_2 oxidation rate observed in these experiments is consistent with an assortment of free-radical processes whose quantitative significance must await model development and testing.

* In reference 15a, SO_2 oxidation was simulated for initial reactant concentrations (ppm) of: $[NO]_o = 0.075$; $[NO_2]_o = 0.025$; $[CO]_o = 10$; $[CH_4]_o = 1.5$; $[C_4H_8]_o = 0.10$; $[CH_2O]_o = 0.10$; $[CH_3CHO]_o = 0.06$; (see Table 2, page 18). In reference 15b, more recent kinetic data were used to predict an SO_2 oxidation rate of 1.5 percent/hr for the same initial reactant conditions except: $[NO]_o = 0.15$ ppm and $[NO_2]_o = 0.05$ ppm.

In relatively clean air, SO_2 oxidation was most probably caused by trace contamination, but the accountable reactions are yet obscure. The mechanism is probably linked to NO_2 contamination in view of the coincident pattern of O_3 and SO_3 formation. However, the possibility of SO_2 oxidation via photoexcitation of SO_2 cannot be ruled out on the basis of the results collected, and some evidence, indeed, supports the involvement of long-lived excited states of SO_2. Whatever the mechanism, one should not overlook the importance of SO_2 oxidation under these conditions; additional attention in future work should be given to factors affecting the "clean-air rate" as well as the "polluted-air rate".

EXPERIMENTAL METHODS

Large Smog Chamber

Description

With the exception of a series of experiments investigating contamination effects on SO_2 oxidation, all irradiations were conducted in Battelle-Columbus' 17.3-m^3 smog chamber having a surface-to-volume ratio of 2.6m^{-1}; the surface is polished aluminum and FEP Teflon (du Pont). Direct irradiation through 5-mil Teflon windows is provided by a bank of 96 fluorescent blacklamps and 15 fluorescent sunlamps. The photon flux of the blacklamps is distributed unimodally in the uv region, with peak intensity at 370 nm; the sunlamp peak intensity occurs at 310 nm. With all lamps operating, the average intensity in the 290-400 nm region is 3.8×10^{16} photons/cm^2-sec, as determined by o-nitrobenzaldehyde actinometry. Using the method of Tuesday[16], light intensity measurements by NO_2 photolysis yield $k_d = 0.43$ min^{-1}. The sunlamps provide <1 percent of the total energy. In the strong absorption band of SO_2, i.e., below 320 nm, the sunlamp intensity corresponds to about 0.16×10^{15} photons/cm^2-sec, compared with noonday sunlight intensity in the SO_2 band of about 1.4×10^{15} photons/cm^2-sec.[11]

Background air supplied to the chamber is taken through a 10-m stack atop a three-story building and is passed through a purification system which includes a permanganate filter bed, a charcoal filter system, an absolute filter, and a humidification unit. After purification, background total hydrocarbon is generally 2-3 ppmC, with the majority being methane. Nonmethane hydrocarbons are usually <0.5 ppmC (mostly paraffins), NO_x <0.02 ppm, CO <4 ppm, and particles $< 10^3$ cm^{-3}.

Chamber Operation

Prior to certain series of experiments, the chamber's surfaces were thoroughly cleaned by washing with water and sometimes isopropanol-water mixtures. After cleaning, the chamber was dried by continuous purging with purified air.

All irradiations were conducted for about 4 hours. Typically, the chamber was first humidified with deionized, double-distilled water vapor followed by consecutive injections of SO_2, NO, NO_2, propylene, and tracer (perfluoropropane).

Continuous and intermittent sampling of the chamber air together with a small unavoidable leak rate resulted in overall chamber dilution rates of about 10 percent/hr. This sizeable rate is particularly important in interpreting the apparent loss of SO_2 where the SO_2 reaction rate is

considerably smaller than the dilution rate. To determine the dilution rate, an inert fluorocarbon (perfluoropropane) tracer was added to the chamber and monitored by gas chromatography.

Estimations of SO_2 loss due to reactions and sulfate aerosol production were made as follows. For each experiment, the dilution data and the observed SO_2 concentration were fitted to first-order kinetic equations. Simple subtraction of the two rate constants gave a good approximation of the removal rate of SO_2 due to processes other than dilution.

In order to compare SO_2 loss with analytical results for H_2SO_4 aerosol during the course of the experiments, it was necessary to predict aerosol concentrations, taking into consideration both the actual SO_2 oxidation rate and the dilution rate. Assuming that the chamber is a perfectly stirred reactor and that the SO_2 to SO_3 reaction rates are first order in SO_2, the appropriate expression[17] for predicting the SO_2 concentration at any time is given by relationship (A),

$$SO_{3_t} = SO_{2_i}\left[e^{-tk_1} - e^{-tk_1(1 + k_3/k_1)}\right] \qquad (A)$$

where SO_{2_i} = initial SO_2 concentration, t = reaction time, k_1 = dilution rate, and k_3 = SO_2 reaction rate. Predicted values of H_2SO_4 appearing in Table 1 were determined in this fashion.

Small Smog Chamber

Description

The small smog chamber used for investigating the effect of air contamination on SO_2 oxidation has a volume of approximately 200 liters and consists of two 45-cm-diameter by 91-cm-high Pyrex bell jars fastened together with an anodized aluminum ring. A vacuum-tight seal between the bell jars and the aluminum ring is made with a Viton L-ring.

Illumination is normally provided by a circular bank of 34 fluorescent blacklamps. NO_2 photolysis yields $k_d = 0.45\ min^{-1}$. For some experiments, three blacklamps were removed and a row of incandescent sunlamps was substituted. The photon flux of the sunlamps, determined by o-nitrobenzaldehyde actinometry, corresponds to an intensity of 1.5×10^{15} photons/cm^2-sec. The energy of these lamps is distributed bimodally, with peak intensities near 310 and 370 nm. The relative intensity of the peaks favors the 370 nm band by a factor of about 2.5.

Chamber Operation

The advantages of the 200-liter chamber over the larger chamber is the practicality of thoroughly cleaning the system and utilizing ultrapure air. For cleaning, the chamber was dismantled and the Pyrex bell jars scrubbed with soap, rinsed, etched with dilute HF, and rinsed again with large quantities of distilled water.

Several purity grades of air and oxygen were used both for purging the reaction system and for the irradiation experiments. Further purification of the air was undertaken by exposing

it to ultraviolet radiation such that O_3 (~1 ppm) was produced. After a residence period of about 30 minutes, the ozonized air stream was passed consecutively through activated charcoal, soda lime, and an absolute filter. Prior to entering the chamber, the air passed over an SO_2 permeation tube (Metronics, Inc.) maintained at constant temperature. The flow system operated continuously, thereby providing a constant SO_2 concentration in the chamber. The permeation tube was simply bypassed for experiments without SO_2.

The chamber thus was operated dynamically at one atmosphere with a constant air throughput of 1.50 liters/min, a rate in excess of the sampling demands during irradiation. Because of the dynamic process, steady-state approximations were used in interpreting the data. Three parameters – SO_2, O_3, and aerosol volume – were monitored during irradiation. In general, near steady-state values for these parameters were established in ~5 hours. An O_3 instrument was tuned to a sensitivity of 1 ppb. The SO_2 instrument had a sensitivity of about 10 ppb and therefore was not very useful in measuring small changes in SO_2. The electrical aerosol analyzer (TSI Model 3030) was estimated to have a sensitivity corresponding to SO_3 concentrations of about 0.25 ppb.

Because of the greater sensitivity in measuring aerosol compared with SO_2, aerosol production was used to compute the SO_2 oxidation rates in spite of several assumptions necessary in interpreting aerosol data. Thus, under steady-state conditions,

$$\frac{d(SO_3)}{dt} = k_f(SO_2) - k_\ell(SO_3) = 0 \quad , \tag{B}$$

where k_f = velocity constant for SO_2 to SO_3 conversion and k_ℓ = velocity constant for SO_3 losses. Taking some typical steady-state data and rearranging relationship (B),

$$k_f = \frac{k_\ell(SO_3)}{(SO_2)} = \frac{(0.45\ hr^{-1})\ (8.7\ ppb)}{(410\ ppb)} = 0.0095\ hr^{-1} \text{ or } 0.95 \text{ percent/hr.} \tag{C}$$

Calculation of the SO_3 concentration and the rate constant for SO_3 loss requires additional explanation. First, the volume of aerosol equivalent to a particular concentration of SO_3 was inferred from measurements of the concentration of aerosols over 10 size intervals using an electrical aerosol analyzer whose operation and calibration have been reported elsewhere.[18] In inferring a volume concentration from the integrated size spectrum, two assumptions are made – one, that all the aerosol volume is in the size range measured, and two, that all the aerosols are perfect spheres. In equating aerosol volume with sulfuric acid concentrations, it is further assumed that equilibrium exists between the condensed and vapor phases of aqueous sulfuric acid ($SO_3 \cdot xH_2O$). Acid mole-fraction and density data[19] were used to convert aerosol volume to SO_3 vapor concentrations at the respective relative humidities. In the exemplary data given above, the aerosol volume concentration was 26.8 $\mu m^3/cm^3$ which, when adjusted for H_2O constituency at a relative humidity of 1 percent, yielded 8.7 ppb (vol/vol) SO_3.

This method of analysis for SO_3 was checked by making simultaneous measurements of H_2SO_4 aerosol with the aerosol analyzer and a chemical method. Microliter quantities of 98 percent sulfuric acid were evaporated in the 17.3-m^3 smog chamber. Upon saturation, nucleation of H_2SO_4 aerosol commenced and growth continued by condensation and coagulation. After a fairly stable distribution of aerosol was established, filter samples were withdrawn for chemical analyses (barium chloranalate method) and the results were compared with SO_3 concentrations calculated in the manner just described from aerosol measurements. The agreement

between the two methods was good – within 10 percent of each other. Thus, in instances where aerosol is composed largely of sulfuric acid of appropriate size, the aerosol volume concentration is probably a fairly accurate measure of SO_2 oxidation.

The second consideration to the $k(SO_3)$ term in relationships (B) and (C) is the velocity constant for aerosol loss. At steady state (where the rate of aerosol formation equals the rate of disappearance), the rate of aerosol loss is given approximately by relationship (D):

$$\frac{-dn}{dt} = k_c n^2 + k_p n + k_w n \quad . \tag{D}$$

where k_c is the second-order constant for coagulation, k_p is the constant for the dynamic flow, and k_w is the constant for wall losses. In the present analysis we are interested only in the change in aerosol mass, so the coagulation term can be neglected since mass is conserved in the process.

The rate constant for the chamber throughput is simply the flow rate/reactor volume, which is 1.25×10^{-4} sec^{-1} for the conditions employed; perfect mixing is assumed.

The appropriate constant for the wall-loss term is far less precise. It is well accepted that inertial deposition of submicron aerosols is nearly zero when the aerosol cloud is not stirred. Therefore, we can assume that wall deposition is purely by diffusion – aerosols are carried to the wall by convective diffusion and deposited thereon by molecular diffusion through a thin boundary layer. Under this condition, the rate of deposition can be approximated by relationship (E):

$$\frac{-dn}{dt} = \left(\frac{SD}{V\delta}\right) n = k_w n \quad . \tag{E}$$

where $\frac{S}{V}$ is the surface to volume ratio of the reactor, D is the aerosol diffusivity, and δ is the thickness of the boundary layer.[20] Data on δ compiled by Fuchs indicate that 20 μm is a useful estimate for aerosols about 0.1 μm diameter. Using that value and the appropriate values of S, V, and D, we have estimated the wall loss constant (k_w) for various particle sizes relative to the constant for flow rate (k_p). The ratios of $(k_w + k_p)/k_p$ indicated below are probably maxima for particle diameters <0.1 μm, because δ was kept constant in computing k_w and, in reality, it increases with increasing coefficient of diffusivity (decreasing particle size):

Particle Diameter, μm	$(k_w + k_p)/k_p$
0.001	14
0.005	1.54
0.01	1.14
0.05	1.01
0.10	1.00

It is obvious from this exercise that wall losses relative to throughput losses will be substantial for aerosols <0.01 μm diameter. During the early period of irradiation where embryonic clusters are formed by nucleation processes, wall losses are no doubt very serious. However, as irradiation proceeds, aerosol growth continues and a much different size distribution of aerosol exists as

steady-state conditions are approached. A representative distribution of particles at steady state is indicated in Figure 1. Sulfuric acid aerosol generated at this time is condensing almost exclusively on existing aerosols, as reflected by the aerosol volume distribution in Figure 1. Thus,

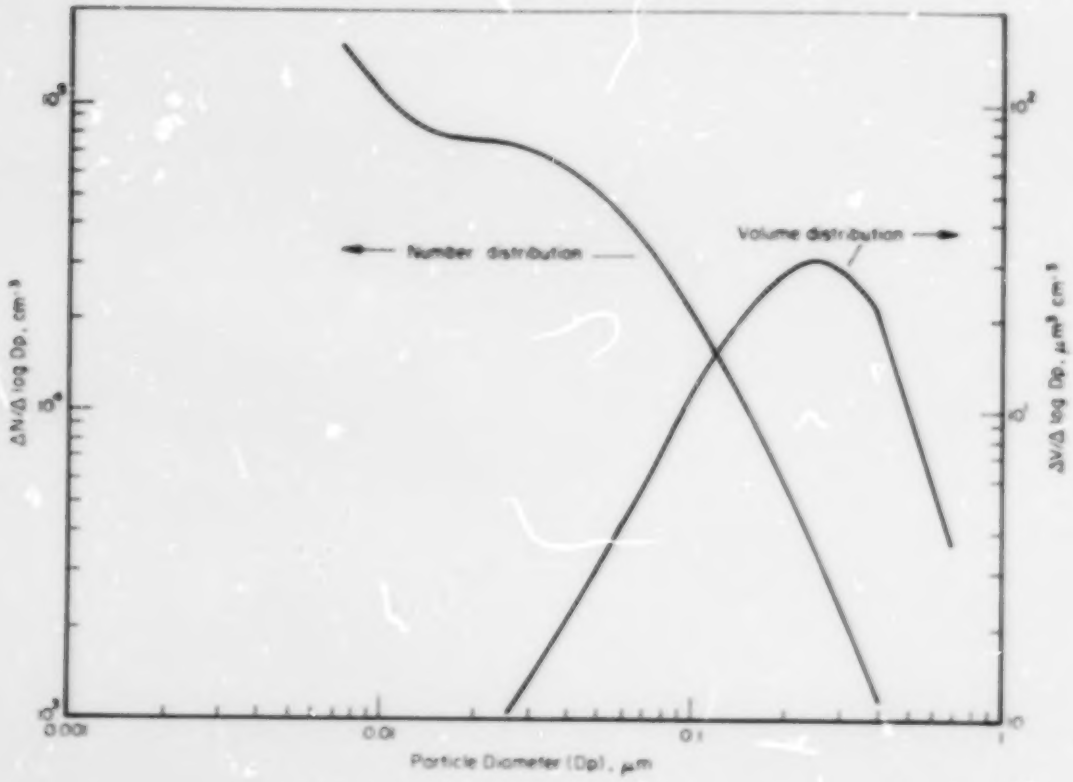

FIGURE 1. SIZE DISTRIBUTION OF $SO_3 \cdot \chi H_2O$ AEROSOL WHERE AN SO_2-AIR MIXTURE IS IRRADIATED 4 HOURS IN A DYNAMIC REACTOR

after several hours of irradiation it appears reasonable to represent the total loss of sulfur acid aerosol in these experiments by the flow rate. This hypothesis was substantiated experimentally by turning off the lamps and observing a decay rate of aerosol volume in accord with the chamber flow rate. This being the case, the steady-state relationship (Relation B) used to compute the SO_2 oxidation rate is justified.

Methods of Chemical Analysis

The following analytical methods were used in monitoring gaseous reactants and products.

Compound	Method
Total hydrocarbons	Flame ionization (Beckman 109 THC monitor)
Propylene and perfluoropropane	Gas chromatography-flame ionization (Varian 2800 GC)
NO and NO_2	Automatic Saltzman (Beckman Air Quality (Acralyzer), dichromate oxidizer for NO
SO_2	Coulometry (Beckman 906) and flame photometry (Tracor, Inc.)
O_3	Chemiluminescence (Battelle-built)
H_2O	Dew pt. (Cambridge Systems, Inc., hygrometer)

Sulfuric acid aerosol was determined in two ways. The least specific but most sensitive method involved the TSI aerosol analyzer discussed earlier. Sulfuric acid was also determined using the barium chloranilate method.[21,22] Aerosol from the smog chamber was collected on 25-mm Nuclepore filters or on 25-mm fiber-glass filters which had been prewashed by refluxing with water and methanol. It appeared that some improvement in collection efficiency was obtained using the glass filters. Neither type was found to suffer any interference due to SO_2 absorption.

The H_2SO_4 aerosol was extracted with an 80 percent isopropanol/20 percent water solution to which excess barium chloranilate (barium salt of 2,5-dichloro-3,6-dihydroxy-p-benzoquinone) was added and the precipitate centrifuged after frequent stirrings. The reaction occurring is

$$BaC_6Cl_2O_4 + H^+ + SO_4^= \rightarrow BaSO_4 + HC_6Cl_2O_4^- \qquad (1)$$

The acid chloranilate anions give a pink color, which is read at 310 nm with a spectrophotometer.

At the conclusion of one experiment (No. 13) a large aerosol collection was made by evacuating the chamber contents through a 10-cm quartz-fiber filter, which was analyzed for total sulfate. The filter was leached in 100 ml of hot water for 16 hours, filtered, and adjusted with $HClO_4$ to a pH of 3.0. A 10-ml aliquot was taken and diluted with 40 ml of isopropanol. Two drops of thorin were added and the $SO_4^=$ titrated with 0.01 N barium perchlorate from a microburet; a yellow-to-pink color change marked the end point. The total sulfate analysis indicated only 24 ppb SO_3, compared with 45 ppb by the barium chloranilate method, 51 ppb by gravimetric analysis of the same filter sample (assuming 100 percent H_2SO_4 aerosol), and a predicted concentration of 42 ppb based on SO_2 depletion. There was no apparent reason for the discrepancy between the two sulfate techniques. The coincidence of the barium chloranilate and gravimetric results, together with the good agreement between the barium chloranilate and the electrical aerosol analyzer results with pure H_2SO_4, led to the establishment of the chloranilate method for routine analysis.

RESULTS AND DISCUSSION

A summary of the pertinent reaction conditions and experimental results of this program is given in Table 1. Before discussing the results, it may be helpful to expand on the meaning of

TABLE I. SUMMARY OF EXPERIMENTS ON SO_2 OXIDATION IN SIMULATED SMOG

Run	Run Description[a]	Initial Concentrations: NO_2, ppb	NO, ppb	C_3H_6, ppbC	RH, percent	NO_2 (D_{max}), ppm-min^{-1}	O_3 Max, ppb	Dilution (D_1), hr^{-1}	(No NO_2 Loss Corr. NO_2 Loss (D_2), hr^{-1}	Corr. NO_2 Loss (k_2=k_2'+D_1), hr^{-1}	Product Concentrations, Formation Rate: $SO_4^=$ Predicted Max[b], ppb	$SO_4^=$ Max[c], ppb	Aerosol Vol. Max[d], μm^3-cm^{-3}	Aerosol $SO_4^=$ Max[e], ppb
	Section A: SO_2 wall loss:													
1	Clean surfaces/dark	660	--	--	31	--	--	0.129	0.193	0.065	[f]	--	--	--
2, [g]	Conditioned surfaces/dark	640	--	--	60	--	--	0.104	0.095	0.011	12	--	--	--
	Section B: SO_2 oxidation in polluted air - preliminary runs													
12	High SO_2	460	690	3,310	61	11	650	0.090	0.129	0.039	40	9	--	--
13	Polluted air NT high SO_2	490	970	3,370	36	12	800	0.119	0.140	0.022	42	65	--	--
9	Low SO_2	120	440	2,640	59	10	300	0.079	0.084	0.005	3	<5	--	--
	Section C: SO_2 oxidation in unpolluted air													
10	Sunlight irradiation	690	0	0	29	--	<5	0.114	0.129	0.014	17	10	13	0
17	Blacklamp irradiation	690	0	0	32	--	60	0.092	0.119	0.026	35	20	300	60
7	Pre-irradiated air	320	<10	--	36	--	60	0.092	0.124	0.032	37	60	--	--
14	Ambient air	360	20	--	60	--	60	0.089	0.134	0.044	66	33	--	--
	Section D: Contaminant investigation of SO_2 oxidation													
2:9	Zero air/200-liter chamber[h]	0	0	0	<2	--	3×10	--	--	--	--	--	<1	0
2:12	Zero air + SO_2/200-liter chamber/sunlamps	410	0	0	<2	--	9	--	--	0.004[i]	--	--	27	30
2:13	Zero air + SO_2/200-liter chamber/blacklamps	410	0	0	<2	--	13	--	--	0.004[i]	--	--	32	30
	Section E: SO_2 oxidation in polluted air - model smog													
19	High C_3H_6/high RH/no SO_2/blacklamps	0	530	4,150	61	12	620	0.087	--	--	0	--	35	0
22	Low C_3H_6/low RH/blacklamps	350	640	1,120	42	4	230	0.112	0.190	0.081	27	<5	235	27
20	Low C_3H_6/low RH/blacklamps	420	690	1,570	41	4	370	0.107	0.192	0.085	30	<5	170	30
21	Low C_3H_6/high RH/blacklamps	440	690	1,580	59	5	290	0.116	0.144	0.028	20	<5	100	21
26	Low C_3H_6/high RH/blacklamps	450	690	1,440	58	5	320	0.139	0.169	0.031	20	<5	105	21
23	High C_3H_6/low RH/blacklamps	670	690	3,120	41	10	490	0.108	0.129	0.021	20	5	300	60
27	High C_3H_6/low RH/blacklamps	480	690	2,800	38	10	350	0.123	0.139	0.015	10	5	200	40
24	High C_3H_6/high RH/blacklamps	410	660	3,130	63	12	370	0.136	0.169	0.041	30	25	200	30
25	High C_3H_6/high RH/blacklamps	490	690	3,060	62	15	360	0.137	0.175	0.038	41	25	290	57

(a) All experiments conducted under fluorescent-sunlamp and blacklamp irradiation in a 17.6-m^3 smog chamber unless otherwise specified.
(b) $SO_4^=$ concentration predicted on the basis of the rate of decay of SO_2, four-order conversion to $SO_4^=$, and 6-hour irradiation time.
(c) Barium chloranilate procedure.
(d) Total aerosol volume concentration inferred from aerosol size distributions determined by Thermo-Systems Inc. air quality analyzer.
(e) $SO_4^=$ concentration assuming total aerosol volume is sulfuric acid, corrected for equilibrium water content.
(f) Underlined values correspond to hypothetical situations.
(g) Average of two very similar experimental conditions and results.
(h) Average of six experiments utilizing "zero air" with and without additional purification.
(i) Calculated from steady-state aerosol concentration assuming all aerosol is sulfuric acid from SO_2 oxidation.

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subheadings appearing in the table. In addition to the abbreviated descriptions in the first column, experimental details of each run are presented in the ensuing discussion. Presumably, the columns of initial concentrations are straightforward. Continuing from left to right, the next column represents the maximum rate of NO to NO_2 oxidation, and the O_3 maximum is either the maximum O_3 concentration or the final O_3 concentration in instances where O_3 was still increasing at the end of irradiation (4 hours). The dilution rate (k_1) is the average rate at which the chamber contents were replenished with clean air. The observed SO_2 loss rate (k_2) is based on the measured SO_2 concentration, and the corrected SO_2 loss rate (k_3) is the measured SO_2 loss rate corrected for the dilution rate. The predicted $SO_4^=$ concentration is the $SO_4^=$ concentration calculated at 4 hours of irradiation from the corrected SO_2 oxidation rate and the chamber dilution rate. The next sulfate column is the sulfuric acid concentration at 4 hours of irradiation, as determined by wet-chemical analysis. The aerosol-volume column is the total aerosol concentration (by volume) at 4 hours as determined by the electrical aerosol analyzer, and the final column corresponds to the sulfuric acid concentration calculated from the total aerosol volume and $SO_3 - H_2O$ equilibria data. Details regarding these parameters were presented in the Experimental Section.

To contribute to the EPA effort on modeling SO_2 oxidation in smog, all the continuous and intermittent chemical data regarding Experiments 20-28 were transcribed onto magnetic tape, which in turn was delivered to the Project Officer. Results on the modeling aspects of the program will be reported separately in a future report.

SO_2 Wall Losses

At the outset of this program, it was necessary to determine the extent to which SO_2 was removed from the experimental system due to interactions with smog-chamber surfaces. The rate of SO_2 removal was measured while SO_2 and clean air were contained in the unirradiated chamber for 4 hours. Measurements were made under two conditions: (1) with chamber surfaces which had been washed with water and dried by purging with clean air and (2) with chamber surfaces which had been "conditioned" by irradiating propylene-NO_x-SO_2 mixtures in air. As indicated in Section A of Table 1, the SO_2 removal rate, corrected for dilution, was 0.5 percent/hr with washed surfaces and about 1.1 percent/hr for conditioned surfaces. It is not certain whether this difference is due to an actual surface effect or is just representative of the uncertainty in measuring the SO_2 depletion rate.

If one had assumed that the losses of SO_2 in these cases were due to gas-phase oxidation rather than wall-removal processes, one would expect to find 5 ppb and 13 ppb H_2SO_4 aerosol, respectively, at the end of 4 hours, having corrected for dilution in the manner noted above. As we shall see, this SO_2 removal rate is substantial compared with the rate of SO_2 removal attributed to SO_2 oxidation under various irradiation conditions, but the wall-loss rate was *not* taken into consideration in computing the "corrected SO_2 loss rate" (Column 9, Table 1) because it was felt to be too uncertain to assign a constant rate to a process which might vary with chamber history or reaction conditions. Thus, in considering the "corrected SO_2 loss rates" in subsequent discussions, it should be kept in mind that the rates are maximums, corrected only for dilution losses, and may be high by perhaps 1 percent/hr.

SO_2 Oxidation in Polluted Air – Preliminary Experiments

In addition to the surface-loss determinations, preliminary experiments were conducted with propylene-NO_x-SO_2-air mixtures to determine the sensitivity of the SO_2 oxidation rate to pollutant concentrations. Experimental conditions and results are summarized under Section B in Table 1. In the experiment in which 480 ppb SO_2 was irradiated with about 490 ppb NO_x and 3300 ppbC propylene, the rate of SO_2 oxidation based on SO_2 removal was 3.9 percent/hr. In this case, the chemical analysis for sulfate aerosol was much lower than the amount computed from SO_2 decay and was likely to be incorrect. In the next experiment at the same SO_2 concentration but nearly double the pollutant (propylene-NO_x) concentration, the SO_2 oxidation rate was 3.2 percent/hr, slightly less than the preceding rate. In the third experiment, in which the initial SO_2 concentration was lowered to 120 ppb, the fraction of SO_2 lost and the amount of sulfate formed were too small to permit reliable calculations of the oxidation rate. Tentative conclusions from this preliminary work were as follows:

(1) The effects of varying pollutant concentrations on SO_2 oxidation appeared small.

(2) The SO_2 oxidation rate could not be obtained reliably at SO_2 concentrations near 100 ppb in the propylene-NO_x-system.

(3) The accuracy in determining the SO_2 oxidation rates would be limited to state-of-the-art techniques in SO_2 and SO_3 analyses.

SO_2 Oxidation in Unpolluted Air

As part of the preliminary work, it was observed that SO_2 was apparently oxidized in clean (i.e., unpolluted) air at rates similar to those observed in air intentionally polluted with propylene and NO_x. For example, with full irradiation (sunlamps plus blacklamps), the rate of SO_2 removal was 3.9 percent/hr in a mixture of propylene and NO_x in air (Run 13) and 4.2 percent/hr in air without these pollutants (Run 7). This disconcerting finding led to some additional investigations with unpolluted air, which are summarized here. Investigations were also conducted with ultrapure air in a 200-liter chamber, and those results are discussed shortly.

In Run No. 16 (Section C, Table 1), 490 ppb SO_2 was irradiated in otherwise unpolluted air* – i.e., air which is typically present in the smog chamber after passing through a purification train. In this case, irradiation was provided only by fluorescent sunlamps. As discussed earlier, the sunlamps provide only about 1 percent of the ultraviolet (290-400 nm) energy of the chamber's blacklamps but about 15 percent of the energy in the strong absorption band of SO_2. Under these irradiation conditions, the SO_2 loss rate was 1.4 percent/hr, or only slightly above the rate that might be attributed to wall absorption of SO_2. Chemical analysis did indicate the presence of sulfate, but the aerosol volume determinations with the mobility analyzer indicated only a trace amount of aerosol. Due to the weak irradiation intensity of the sunlamps, the results of this experiment are inconclusive with respect to the importance of SO_2 excitation to SO_2 oxidation.

* Typical contamination levels of this air are 1.5-2.5 ppm CH_4, <0.5 ppmC nonmethane hydrocarbons (mostly paraffins), <0.02 ppm NO_x, 2-4 ppm CO, and <1000 particles/cm^3.

A similar experiment (No. 17) was conducted with blacklamp irradiation. The SO_2 loss rate was 2.6 percent/hr, and the chemical analysis for sulfate was near the sulfate level predicted by SO_2 removal.

The third experiment (No. 7) in this section was similar to the previous one, except that SO_2 was admitted to the chamber after the air had been "photochemically exhausted" by irradiating it for 65 hours. During the first few hours of the preliminary irradiation, about 25 ppb O_3 appeared, and within the next few hours it diminished to some steady-state concentration below the detection limit (<10 ppb). Upon introducing SO_2 at the 65th hour, O_3 increased steadily to a maximum value of 40 ppb as in the previous run. The SO_2 decay rate during this period was 4.2 percent/hr, and the measured sulfate concentration was in fair agreement with the predicted concentration.

In the fourth experiment described in Section C (No. 14), 540 ppb SO_2 was irradiated in ambient air. Unfiltered air from outside the laboratory was pulled into the chamber early in the morning. The air that morning was unusually clean for Columbus, containing 20 ppb NO, 0.4 ppm nonmethane hydrocarbon, 4 ppm CO, 2×10^4 particles/cm^3 and having a light-scattering (b scat) value of $0.8 \times 10^{-4} m^{-1}$. Irradiation of this mixture also produced 40 ppb O_3, and SO_2 was removed at the rate of 4.4 percent/hr.

In summary, we observed an SO_2 oxidation rate of about 3 percent/hr (corrected for a presumed SO_2 wall-loss rate of about 1 percent/hr) upon blacklamp irradiation of relatively clean air – i.e., both laboratory and ambient air. This finding is highly important if SO_2 excitation and/or trace contamination of the air is responsible for the observed rate. On the other hand, if the observed oxidation rate is a manifestation of some surface condition, it may or may not be important, depending on the nature of the surface effect. These possibilities are considered further in light of limited data.

A potentially influential factor in these experiments is the condition of the smog-chamber's surfaces. It is conceivable that hydrocarbons, nitrites, aldehydes and organic acids contaminate the chamber surface, and some of these compounds could generate reactive species by various photodissociation processes. For example,

$$H_2CO + h\nu \rightarrow HCO + H \quad (2)$$

$$RCHO + h\nu \rightarrow R + HCO \quad (3)$$

$$HONO + h\nu \rightarrow HO + NO \quad (4)$$

$$RONO + h\nu \rightarrow RO + NO \quad (5)$$

Accumulation of condensed matter on the chamber surface does not seem to be crucial, however. Experiment No. 16 was conducted immediately after the chamber's surface was cleaned by scrubbing with water, and the SO_2 oxidation rate was not much different from that observed in all the other experiments in which the surfaces had been exposed to repeated smog irradiations. Thus, it appears that surface contamination had little effect on the observed SO_2 oxidation rates.

Characterization of trace contamination of air (contamination levels lower than those commonly found in the atmosphere) is problematic in that it is not practical to conduct analysis for contaminants when one is not sure what species to look for. Furthermore, it is not practical to extensively purify the volume of air needed to purge and occupy a large smog chamber. To further investigate the possibility of contaminant effects, irradiations were conducted in a small (200-liter) chamber where extensive air purification was possible. Those results, discussed in the succeeding section, indicate that trace contamination may be a factor in SO_2 oxidation even when extensive air purification was performed, but they do not conclusively identify the contaminant(s).

In the large chamber, where air purification is incomplete, the most likely contaminant which would initiate SO_2 oxidation at the outset of irradiation is nitrous acid (HONO). Nitrous acid would form at low concentrations in equilibrium with H_2O and traces of NO and NO_2, and it photolyzes (Reaction 4) to yield HO radicals which add to SO_2. Although the course of the $HOSO_2$ radical in subsequent smog reactions is uncertain, it has been proposed that the specie most likely adds to molecular oxygen (giving $HOSO_2O_2$) which in turn oxidizes NO to NO_2 in an analogous fashion with HO_2 and RO_2.[15b,23] Thus, under some circumstances, inclusion of SO_2 in smog reactions might enhance rather than suppress ozone formation by increasing the chain length of NO to NO_2 conversion. Evidence of such participation is seen in the prolonged experiment with "photochemically exhausted" air (Run No. 7). Presumably, after 65 hours of irradiation, the chain length for NO to NO_2 conversion was quite short because most of the species capable of oxidizing NO have been consumed over this period. Upon introducing SO_2 after 65 hours, the concentration of ozone gradually increased in accord with the chemistry discussed.

Contaminant Experiments

The preceding results prompted additional investigations in a 200-liter Pyrex chamber where surfaces could be readily cleaned and ultrapure air would be used routinely. Fine tuning of a chemiluminescent monitor made possible the detection of ozone with a sensitivity of 1 ppb. SO_2 was monitored with a Beckman 906 Analyzer and aerosol was monitored with a TSI Model 3030 Electrical Analyzer. Details on the operation of the chamber and the methods of interpreting the data were described earlier.

The original plan in these experiments was to begin with a system clean enough to produce no detectable smog manifestations when irradiated and then to add contaminants to either the surface or the air to produce SO_2 oxidation effects. Six experiments were conducted with chamber surfaces which had been acid etched (HF), rinsed with deionized double distilled water, and subsequently exposed only to clean air. Air ranging in quality from ordinary breathing air to ultrapure air (Air Products UPC grade: CH_4 < 0.1 ppm, CO < 1 ppm) was irradiated alone and, in most cases, upon further purification by ultraviolet exposure, charcoal, soda lime, and absolute filters. Under all conditions, both sunlamp and blacklamp irradiation produced ozone (3 to 10 ppb) after several hours of exposure. The buildup of ozone was always gradual, indicative of chain-reaction processes. For brevity, the series of experiments with various grades of "zero air" is represented under Section D of Table 1 as a single experiment (Run No. 209), and the range of ozone observed is indicated. In every case, the aerosol volume concentration was less than the detection level estimated at 1 $\mu m^3/cm^3$.

Experiments No. 202 and 203 were conducted with 410 ppb SO_2 in zero-grade air. As in the experiments without SO_2, both sunlamp and blacklamp irradiation were used. For the 200-liter chamber, blacklamp irradiation intensity is about 20 times as great as the sunlamp intensity in the 290-400 nm region, but in the strong absorption band of SO_2 the sunlamp intensity is slightly greater than the blacklamp.

With blacklamp irradiation (Run No. 203), the rate of SO_2 oxidation inferred from aerosol determinations was 0.4 percent/hr, and 11 ppb ozone was present at steady state. With sunlamp irradiation (Run No. 202), the SO_2 oxidation rate was nearly 0.9 percent/hr, and the ozone concentration at steady state was 9 ppb. These results, coupled with the relative energy distributions of the lamps, strongly suggest a shorter wavelength dependence on the SO_2 oxidation process. This dependence is not likely if NO_2 were the only absorbing specie important to SO_2 conversion. If photoinduced SO_2 excitation is involved, crude extrapolation of these data to conditions of atmospheric sunlight would increase the observed oxidation rate by a factor of at least 2, or to nearly 2 percent/hr

In spite of qualitative evidence supporting the participation of excited SO_2, the appearance of ozone in the experiments without SO_2 proves that the air is contaminated and precludes any unambiguous interpretation of the results.

SO_2 Oxidation in Polluted Air – Model Smog

To establish an initial data base for work on modeling SO_2 conversion in smog, eight irradiation experiments were conducted using propylene-NO-NO_2-SO_2-H_2O-air mixtures. Originally, replicate experiments were planned at constant NO_x concentrations and two concentrations of propylene, SO_2, and H_2O. However, SO_2 was hence excluded as a variable in view of preliminary experiments showing uninterpretable results at low concentrations of SO_2.

For convenience, the eight experiments are arranged in Table 1, Section E, as pairs, but the sequence of conducting the experiments was selected at random to avoid any bias that might be inherent in day-to-day operation. Also, unlike the preliminary experiments, irradiation in this series was provided only by fluorescent blacklamps to minimize the lamp intensity in the strong absorption band of SO_2 and thereby minimize the possibility of reactions attributable to SO_2 excitation.

Experiment 19 (Table 1, Section E) *without* SO_2 was conducted to determine the aerosol yield attributable to propylene-NO_x-H_2O reactions. This was of interest because aerosol produced in similar experiments with added SO_2 was interpreted as being derived solely from SO_2. As indicated in Table 1, a small volume of aerosol was produced in this case relative to those in which SO_2 was present. And, because the propylene and NO_x concentrations were higher in Experiment 19, the contribution of aerosol from propylene-NO_x reactions was probably even smaller in Experiments 20-28.

In the model experiments at the lower propylene-to-NO_x ratio of about 1:1, a relative humidity change from 40 to 60 percent nearly doubled the maximum rate of NO oxidation. The higher humidity seemed to have a small positive effect on the overall SO_2 oxidation rate calculated from SO_2 depletion. In all four experiments the analysis for sulfuric acid aerosol was below the detection limit (5 ppb); presumably, the sulfate aerosol was in some other form. Subsequent chemical analyses indicated that the sulfate was probably combined as $(NH_4)_2SO_4$.

At the higher propylene-to-NO_x ratio of 2/1, the NO oxidation rate increased only about 40 percent in changing the relative humidity from 40 to 60 percent. (As expected in experiments at comparable humidities, the higher propylene-to-NO_x ratio resulted in higher NO oxidation rates and ozone yields.) The higher humidities at propylene/NO_x ratios of 2/1 increased the SO_2 oxidation rate in terms of the overall SO_2 loss to a greater extent than that observed in the experiments at lower HC/NO_x ratios. Thus, it appears that the SO_2 oxidation rate is affected by relative humidity and HC/NO_x ratios by varying degrees and perhaps in some interrelated ways. Reactions likely to be involved in the oxidations are discussed in the next section of the report.

A few comments are in order regarding the reproducibility of the experiments. It would appear that, at least in the instances of measuring NO oxidation, SO_2 and propylene consumption, and ozone formation, that reproducibility varies from good (± 10%) to fair (± 30%). Obviously, the data are too limited to treat statistically, and the value of having replicate data appears to be borne out here.

In assessing the reproducibility of the chemistry associated with these results, one must keep in mind the variability associated with the initial reaction conditions and also that which is linked to the inconsistent dilution rates. For example, the final concentration of ozone (and aerosol as well) is considerably higher in Run 23 compared with Run 27, in spite of similar NO oxidation rates. However, the dilution rate in Run 27 is greater by some 23 percent, which would account for much of the difference in the uncorrected ozone concentrations after 4 hours of irradiation.

Mechanisms of SO_2 Oxidation

It is not an objective of this study to provide direct experimental evidence in support of particular mechanisms of SO_2 oxidation. However, in interpreting results presented here, it is useful to discuss some of the more plausible reaction schemes. First, we will consider the reaction system in which SO_2 was irradiated in air containing propylene and NO_x.

Polluted Air

The pattern of aerosol growth (and, presumably, SO_2 oxidation) in the propylene-NO_x-SO_2 system is indicated in Figures 2 and 3. It is evident that there is a rather short induction period to aerosol growth, followed by a maximum rate of volumetric growth. The "S shape" of the aerosol formation curve is more pronounced in Figure 3, where the propylene/NO_x ratio is twice as great as for the experiment appearing in Figure 2, i.e., SO_2 oxidation is more gradual and extended at lower HC/NO_x ratios. In both cases, onset of the maximum in the rate of SO_2 conversion occurs near the appearance time of ozone when there are nearly equal quantities of NO and NO_2. These general trends in oxidation are consistent with an assortment of free-radical reactions with SO_2, each of which is likely to make a significant contribution to the overall rate. The reactions thought to be most significant are listed in Table 2. Following each reaction is a corresponding SO_2 conversion rate computed by Calvert[15a] for a computer simulated smog system. Although the smog simulation is considerably different from the propylene-NO_x system, it is noteworthy that the sum of the SO_2 oxidation rates of 2-3 percent/hr is in the range observed for oxidation in the propylene-NO_x system.

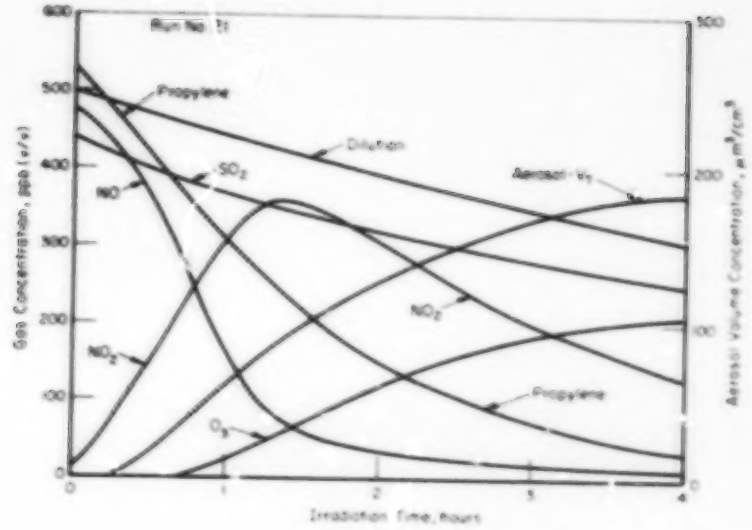

FIGURE 2. SMOG PROFILE OF AEROSOL FORMATION DURING IRRADIATION OF THE C_3H_6-NO-NO_2-SO_2-H_2O MODEL SMOG SYSTEM

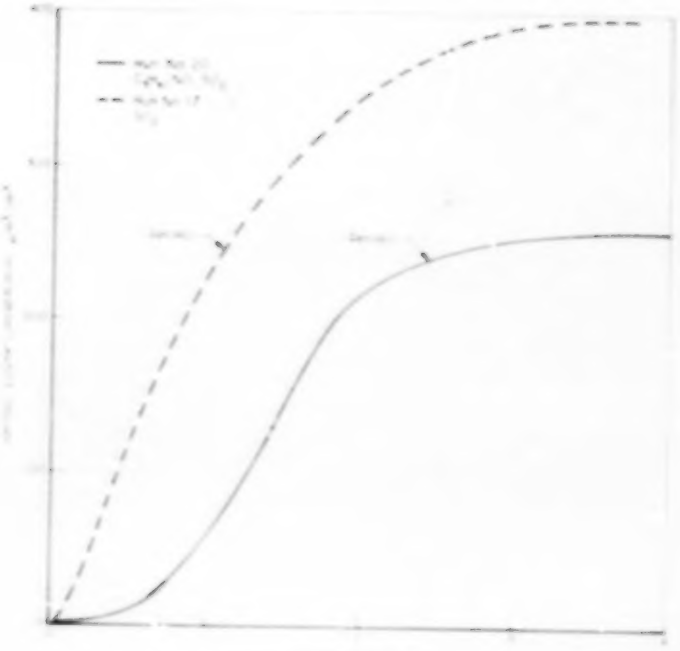

FIGURE 3. PROFILES OF AEROSOL FORMATION FROM SO_2 OXIDATION IN UNPOLLUTED AIR AND IN AIR CONTAINING C_3H_6 AND NO_x

As indicated in Table 2, Reactions 6-8 add an oxygen atom to SO_2, while Reactions 9 and 10 add radicals to SO_2; the products of these reactions convert to sulfuric acid and organic sulfates (esters of sulfuric acid) in subsequent steps. The radical-addition reactions have been less frequently considered than Reactions 6-8 probably because they have not been directly observed in the laboratory. Reaction 9, however, has been studied recently by Wood et al.[13], and they report a rate of about 5×10^{-2} ppm^{-1} min^{-1}. Calvert's estimate of the rate for Reaction 10 is based on rate data for the somewhat analogous reaction of methyl radicals with SO_2, and similarly, estimates for the rate of Reaction 8 are based on data for Reaction 7.

TABLE 2. ESTIMATED RATES OF HOMOGENEOUS SO_2 REACTIONS IN SIMULATED SMOG[15]

Reaction		SO_2 Conversion Rate, percent/hr[a]
(6)	$\cdot CH_2OO\cdot + SO_2 \rightarrow CH_2O + SO_3$	0.4
(7)	$HO_2 + SO_2 \rightarrow HO + SO_3$	0.9
(8)	$RO_2 + SO_2 \rightarrow RO + SO_3$	0.2
(9)	$HO + SO_2 \rightarrow HOSO_2\cdot$	0.2
(10)	$RO + SO_2 \rightarrow ROSO_2\cdot$	0.5
	Total	2.2

(a) Theoretical rates of SO_2 removal occurring in a simulated atmosphere containing the following initial concentrations (ppm): NO_2 = 0.025, NO = 0.075, trans-2-butene = 0.10, CH_2O = 0.10, CH_3CHO = 0.06, CO = 10, and CH_4 = 1.5. The indicated rates correspond to 20 minutes of irradiation in sunlight (z = 40°).

Considerable kinetic data are available on Reactions 6 and 7. Reaction 6 has been investigated by Cox and Penkett[14] in their studies of olefin-O_3-SO_2 reactions in the dark. The intermediate responsible for SO_2 oxidation in this case may be an ozonide of the respective olefin or a "zwitterion", which is shown in Reaction 6 as a diradical. The rate of 0.4 percent/hr appearing in Table 2 is their estimate where propylene is the hydrocarbon precursor of the zwitterion rather than 2-butene, which was employed in the simulated smog system of Calvert. Reaction 7 has recently been reinvestigated by Davis et al.[12], and they report a rate constant of 0.45 ppm^{-1} min^{-1}.

A great deal of uncertainty associated with predicting the extent to which these and other reactions contribute to the overall SO_2 oxidation rate obtains in efforts in establishing the free-radical concentrations in smog simulations. It is anticipated that computer simulations of the propylene-NO_x-SO_2 system in the near future will provide additional information as to the relative importance of these reactions. Until that time, speculation on the quantitative aspects of these reactions is unwarranted.

Unpolluted Air

The most perplexing results of this program are those involving SO_2 conversion in air which was relatively clean compared with polluted air. If we assume as before that the rate of aerosol growth in irradiated SO_2-H_2O-air systems reflects the rate of SO_2 oxidation, one sees in Figure 3 that the maximum aerosol growth rate occurs immediately upon irradiation, with the rate gradually diminishing as the irradiation proceeds. This pattern is obviously different from that of polluted air and may possibly be due to different and/or competitive reaction meachanisms in the two cases.

As discussed earlier, SO_2 oxidation observed in relatively clean air is most likely attributable to trace contaminants in such proportions as to generate higher-than-expected concentrations of reactive intermediates which oxidize SO_2 via mechanism just outlined. At least two alternative reaction schemes can be presented for SO_2 oxidation under such conditions, albeit neither scheme is consistent with all the facts, and considerable skepticism exists among chemists regarding the possible significance of either scheme.

The first argument to be considered is a familar one involving triplet SO_2 ($^3SO_2$) formation, followed by oxygen addition to form some excited state of SO_4 (SO_4^*) and disproportionation to SO_3 and O-atoms[24]†.

$$SO_2 + h\nu \rightarrow {}^1SO_2 \qquad (11)$$

$${}^1SO_2 + M \rightarrow SO_2 + M \quad \text{deactivation} \qquad (12)$$

$${}^1SO_2 + M \rightarrow {}^3SO_2 \quad \text{spin inversion} \qquad (13)$$

$${}^3SO_2 + O_2 \rightarrow SO_4^* \qquad (14)$$

$$SO_4^* \rightarrow SO_3 + O \qquad (15)$$

followed by ozone and sulfuric acid formation

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (16)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (17)$$

A recent study of SO_2 photochemistry which included a high-pressure mechanism of $^3SO_2$ formation leads to a theoretical maximum rate of SO_2 photooxidation in the lower atmosphere of 1.9%/hr.[26] In this study, the concurrence of SO_3 and O_3 formation lend support to the above mechanism. However, no enhancement of the SO_2 oxidation rate was observed in the 200-liter chamber when air was replaced by pure O_2. If chemical rather than physical quenching of $^3SO_2$ by O_2 occurs, as the mechanism implies, then both SO_3 and O_3 would be expected to have increased in pure O_2, and this was not observed.

† Alternatively, SO_4^* might react with O_2 to generate SO_3 and O_3 directly as originally suggested by Blacet.[25] However, this simple reaction scheme involves a different transition state and evidence has been presented to discount its probable occurrence.[24]

A second and perhaps more obscure mechanism which can be postulated involves participation of nonemitting excited states of SO_2 (SO_2^*). These presumably long-lived states have been invoked to account for several photochemical reactions of SO_2 which occur under conditions which preclude as reactants the easily quenched emitting singlet and triplet states of SO_2.[27] An abbreviated mechanism of SO_2 oxidation involving such species follows.

$$SO_2 + h\nu\ (290\text{-}320\ nm) \rightarrow {}^1SO_2 \qquad (11)$$

$${}^1SO_2 + M \rightarrow SO_2^* + M \qquad (18)$$

$$SO_2^* + SO_2 \rightarrow SO_3 + SO \qquad (19)$$

$$SO_3 + SO \rightarrow 2SO_2 \qquad (20)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (16)$$

In this scheme, H_2O and SO might compete for SO_3. Thus, in the absence of H_2O and/or other sinks for SO and SO_3, recombination to SO_2 would result in apparently low SO_3 quantum yields. Reaction 20 was recently invoked[28] to rationalize the divergent quantum yields (Φ_{SO_3}) of previous investigations.[9,10,29]

There are other possibilities for SO reactions. In air, SO might react to form SO_3:

$$SO + O_2 + M \rightarrow SO_3 + M \qquad (21)$$

and on surfaces it is known to form SO_2 and S_2 by an obscure mechanism.

In the proposed scheme (Reactions 18-19), ϕ_{SO_3} is dependent on the SO_2 concentration. In the study of Allen, et al.,[9] a small positive correlation of ϕ_{SO_3} with SO_2 was observed but thought to be an artifact of the experimental procedure. Cox[10] observed a definite dependency of ϕ_{SO_3} on the SO_2 pressure, accounting for it by Reaction 22 and subsequently Reaction 21.

$${}^3SO_2 + SO_2 \rightarrow SO_3 + SO \qquad (22)$$

and rightfully dismissing their importance under atmospheric conditions on the basis that ambient SO_2 concentrations cannot compete with O_2 and N_2 in quenching $^3SO_2$. Thus, a requirement of the SO_2^* argument is that the nonemitting specie be long-lived; i.e., unlike $^3SO_2$, it must survive numerous collisions with N_2 and O_2. Indeed, an important observation in earlier work[27] was that long-lived states of SO_2^* could survive enough collisions with "inert" reacting partners to permit them to ultimately react chemically in the atmosphere.

In conclusion, the observation of SO_2 oxidation rates $\geq$ 1 percent/hr in unpolluted air is certainly important in considering its removal rate on a global basis. The prevailing mechanism(s) of the process are not clear.

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